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Experimental data and modeling of the thermodynamic properties of bread dough at refrigeration and freezing temperatures

T.G. Matuda, P.A. Pessôa Filho, C.C. Tadini*

Food Engineering Laboratory, Escola Politécnica, University of São Paulo, P.O. Box 61548, Zip Code: 05424-970, São Paulo, SP, Brazil

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ABSTRACT

Thermodynamic properties of bread dough (fusion enthalpy, apparent specific heat, initial freezing point and unfreezable water) were measured at temperatures from −40 °C to 35 °C using differential scanning calorimetry. The initial freezing point was also calculated based on the water activity of dough. The apparent specific heat varied as a function of temperature: specific heat in the freezing region varied from (1.7–23.1) J g^{-1} °C^{-1}, and was constant at temperatures above freezing (2.7 J g^{-1} °C^{-1}). Unfreezable water content varied from (0.174–0.182) g/g of total product. Values of heat capacity as a function of temperature were correlated using thermodynamic models. A modification for low-moisture foodstuffs (such as bread dough) was successfully applied to the experimental data.

1. Introduction

The world consumption of bread produced from frozen dough has increased over the past years: the world market for frozen bakery products has increased from US$ 3.16 billion in 2004 to US$ 3.71 billion in 2008 (Euromonitor International, 2009). In the USA alone, the total wheat flour processed for frozen white bread increased from 120 million kg in 1997 to 235 million kg in 2002 (U.S. Census Bureau, 2004). This increase can be ascribed to economic reasons, such as the centralization of manufacturing and distribution, the use of nonspecialized workers and the ready availability of "fresh" bread at sale points (Selomulyo and Zhou, 2007).

Knowledge of thermodynamic properties (such as initial freezing point, fraction of frozen water, specific heat and enthalpy) at refrigeration and freezing temperatures is essential for the efficient design and selection of processes and equipments, estimation of freezing and thawing time, and control of operating costs. However, values of thermal and physical properties of foods strongly depend on temperature and composition (Cogné et al., 2003; Hamdami et al., 2004; Ngadi et al., 2003; Tocci et al., 1997). Although many authors have measured thermophysical properties of bakery products, experimental data for below the freezing point are scarce and do not comprise all composition ranges that may be of interest to the bakery industry – not to mention the inherent variation in properties due to differences in product specification (Hamdami et al., 2004; Lind, 1991; Rask, 1989).

Differential scanning calorimetry (DSC) – along with the corresponding modeling – has already been used to determine thermodynamic properties and their variation with temperature and composition of food materials. Previous studies include the determination of properties of sweet potato (Fasina, 2005), ice cream (Cogné et al., 2003), partly baked bread (Hamdami et al., 2004), dough with ice structuring proteins (Xu et al., 2009), gluten (Bot, 2003), frozen dough with carrot antifreeze protein supplementation (Zhang et al., 2007), pre-fermented frozen bread dough (Baier-Schenk et al., 2005), bread dough (Lind, 1991) and bakery products (Baik et al., 2001). DSC is the number one choice for determining these properties, as it is a rapid and simple tool and a significant amount of information can be obtained through a single thermogram (Cogné et al., 2003). However, DSC has the disadvantage of using a very small sample size, which may result in differences in composition due to the heterogeneity of the material – a significant aspect when food properties are to be measured. Moreover, for determination of initial freezing point (T_f), the use of DSC may be restricted due to the fact that the apparent specific heat curve is usually imprecise near this temperature (Wang and Kolbe, 1991).

Therefore, it is often necessary to complement and/or correct information from the DSC thermogram. In particular, the determination of the initial freezing point can be done via alternative methods such as water activity measurements close to the freezing temperature. The freezing point depression equation

* Corresponding author. Tel.: +55 11 3091 2258; fax: +55 11 3091 2255.
E-mail address: catadini@usp.br (C.C. Tadini).

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Nomenclature

a	constant in Eq. (2)
A	constant in Eq. (8) and Eq. (9)
a_w	water activity
b	constant in Eq. (2) and Eq. (3)
B	constant in Eq. (8) and Eq. (9)
Bi	*Biot* number ($h \cdot r \cdot k^{-1}$), dimensionless
c	constant in Eq. (8) and Eq. (9)
Cp	specific heat [J g^{-1} °C^{-1}, wet basis]
Cp_{app}	apparent specific heat [J g^{-1} °C^{-1}, wet basis]
Cp^*_{app}	dynamic corrected apparent specific heat [J g^{-1} °C^{-1}, wet basis]
h	heat transfer coefficient [W m^{-2} K^{-1}]
H	enthalpy [J g^{-1}, wet basis]
k	thermal conductivity of fresh dough [W m^{-1} K^{-1}]
L	ice fusion latent heat [J g^{-1}]
m	constant in Eq. (8) and Eq. (9)
M	molecular weight [g mol^{-1}]
n	constant in Eq. (8) and Eq. (9)
r	characteristic dimension [m]
R	ideal gas constant [J mol^{-1} K^{-1}]
t	time [s] or [min]
T	temperature [°C] or [K]
T_0	initial freezing point of pure water [°C] or [K]
T_{amb}	ambient temperature [°C]
T_f	initial freezing point [°C] or [K]
T_g	glass transition temperature [°C]
T_i	initial temperature [°C]
T_t	initial thawing point [°C] or [K]
x	mass fraction
α	thermal diffusivity of fresh dough [m^2 s^{-1}]
$\Delta_{fus}H$	fusion enthalpy [J g^{-1}, wet basis]
τ	time constant in Eq. (10) [s]

Subscripts

0	initial
b	bound water
f	freezing
fus	fusion
I	ice
j	different components
s	solids
t	thawing
u	unfreezable water
unf	unfrozen
w	water

permits to determine the freezing point through the water activity value:

$$\frac{d\ln a_w}{dT} = \frac{M_w L}{RT^2} \quad (1)$$

wherein a_w is the water activity, T is the temperature [K], M_w is the molecular weight of water [g mol^{-1}], L is the latent heat of fusion of ice [J g^{-1}] and R is the ideal gas constant [J mol^{-1} K^{-1}]. This equation is valid if the system is in thermodynamic equilibrium at constant pressure and is above its eutectic point. Using Eq. (1), the initial freezing point (T_f) can be estimated (Boonsupthip et al., 2009) and the DSC information can be adequately corrected.

Other properties of interest which can be obtained from the DSC thermogram include the enthalpy, which is used for calculating the total heat and the rate of removal during refrigeration and freezing of food products, and also the amount of unfreezable water, which is the fraction of water unavailable for freezing in a food product at the reference temperature of −40 °C (Fasina, 2005). This information is particularly important to determine storage conditions and the shelf life of frozen food products.

In this work, thermodynamic properties of bread dough such as unfreezable water content, enthalpy of fusion, initial freezing point and apparent specific heat were determined using DSC in a temperature range from −40 °C to 30 °C. Complementary experiments included the determination of initial freezing point through water activity measurement. A nonlinear estimation procedure was used to adjust the experimental data to obtain more accurate predictive models than those presented in the literature.

2. Experimental

2.1. Materials

Commercial bakers' flour (water content 14.20%, protein 9.15%, ash 0.6% and farinograph water absorption 64.60% according to AACC methods (2000)), salt, vegetable shortening, polysorbate 80 (ALINE 800K Oxiteno Nordeste, Brazil), diacetyl tartaric acid esters of monoglycerides (DATEM PANODAN® ALB 10 PS, Danisco, Brazil) and ascorbic acid (Casa Americana, Brazil) were purchased on the local market or donated by producers. Distilled water was used in all formulations.

2.2. Bread dough preparation

Three formulations of bread dough with different water contents were produced from 150 g of wheat flour, 3 g of salt, 1.5 g of vegetable shortening, 0.45 g of polysorbate 80, 0.3 g of DATEM, 0.03 g of ascorbic acid (analytical grade) and water − (57, 60 and 63) % on wheat flour basis. Yeast was not added due to the fact that the fermentation process could hinder the interpretation of the DSC curve results.

All ingredients except salt were mixed (Kitchen Aid, model BEA 52A, USA) for 7 min at low speed until the water had been completely absorbed. Then salt was added and the dough was mixed at a high speed for 30 min until completely developed. The temperatures of the ingredients and the final temperature of the dough were monitored. Fresh dough samples were collected for water content, DSC and water activity analyses.

2.3. Water content

The initial water content (x_{w0}) of the bread dough was determined in two stages in four replicates according to AACC method 44-15A (AACC, 2000).

2.4. Water activity

The water activity (a_w) of each bread dough formulation was determined in triplicate at 25 °C using an electronic dew-point hygrometer (Novasina, AW-Center Serie AWC 500, Switzerland), ideally the water activity should be measured as close as possible to the freezing point temperature. The initial freezing point (T_f) was determined through Eq. (1).

2.5. Time–temperature curves

Previously prepared bread dough cylinders (diameter: 4.5 cm, length: 10 cm, weight: 200 g) were packed with plastic film and

immediately submitted to freezing in a horizontal freezer (Metal Frio, DA400, Brazil) at −18 °C. The temperatures at the center of the bread dough cylinder and the ambient were monitored (in triplicate) by thermocouples during the freezing process. Data was acquired with a National Instruments interface, a computer and LabView 5.1 software (National Instruments, USA). Some pieces were thawed at 18 °C and both temperatures (core piece and ambient) were monitored. The initial freezing point (T_f) was determined from cooling curves and the initial thawing point (T_t), from heating curves according to the extrapolation method described by Rahman et al. (2009).

2.6. Thermodynamic properties

DSC experiments were conducted for each formulation using a differential scanning calorimeter DSC 2010 (TA Instruments, USA) calibrated with indium (melting point = 156.61 °C; $\Delta_{fus}H$ = 28.54 J g^{-1}) and water (melting point = 0 °C and $\Delta_{fus}H$ = 333.5 J g^{-1}). To avoid water condensation, nitrogen gas was continuously flushed through the calorimeter head at a rate of 45 mL min^{-1}. Samples (12–16) mg were placed in a hermetic aluminum pan (20 μL), which was placed inside the calorimeter and frozen with liquid nitrogen to a temperature of −50 °C. The samples were then heated to 40 °C at a heating rate of 5 °C min^{-1}. An identical empty pan was used as reference and all experiments were conducted in triplicate.

The apparent specific heat (Cp_{app}) and enthalpy (H) were calculated by Universal V2.5H software provided by the manufacturer. Experiments were also conducted with distilled water. In this case, the freezing peak was adjusted to 0 °C, which corresponds to the initial freezing point of water, using the methodology presented by Wang and Kolbe (1991).

2.7. Statistical analysis

Using the statistical program Statgraphics Centurion XV (StatPoint, Inc., USA), analysis of variance (ANOVA) was applied to the results obtained for water content, unfrozen water content and enthalpy of fusion within a 95% confidence interval. A nonlinear estimation procedure was used for minimizing the sum of squared errors (SSE) between experimental and predicted data.

3. Results and discussion

3.1. Experimental results

By making the hypothesis that frozen bread dough consists of three phases (an aqueous solution, insoluble solids and ice), it is possible to calculate the bound water fraction and the enthalpy change upon freezing from the DSC curves as a function of temperature.

The apparent specific heat (Cp_{app}) of bread dough formulated with different water contents is presented in Fig. 1. In the temperature range from (−20 to 0) °C, where there is a phase change, the value of Cp_{app} increased abruptly from (2–15) J g^{-1} °C^{-1}.

The total enthalpy, including both sensible heat and latent heat of fusion, was directly calculated through numerical integration of Cp_{app} as a function of temperature, using the reference temperature of −40 °C for zero enthalpy (Chen, 1985; Pham, 1987; Tocci et al., 1997) according to Eq. (2):

$$H = a + Cp_{app}(T) \times T - \frac{b}{T} \tag{2}$$

wherein H is the total enthalpy [J g^{-1}], $Cp_{app}(T)$ is the apparent specific heat of frozen dough as a function of temperature

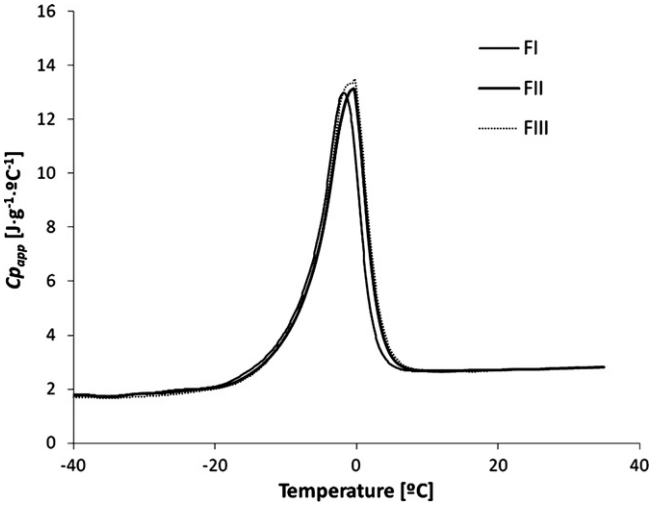

Fig. 1. Apparent specific heat of frozen bread dough (Cp_{app}) with different initial water contents (FI: 0.422 g/g total product; FII: 0.433 g/g total product; FIII: 0.443 g/g total product), obtained from DSC curves.

[J g^{-1} °C^{-1}], the term $Cp_{app}(T)\times T$ is the sensible heat component, $-b/T$ is the latent heat component and a is an integration constant depending on the reference temperature. The constant b can be determined through Eq. (3), derived from Raoult's law:

$$b = \frac{M_w}{M_s}\frac{x_s R T_0^2}{M_w} \tag{3}$$

wherein M_w is the molecular weight of water [g mol^{-1}], M_S is the effective molecular weight of soluble solids [g mol^{-1}], x_s is the soluble solids fraction [g/g product], R is the gas constant [8.31 J gmol^{-1} K^{-1}] and T_0 is the absolute temperature of water at 0 °C [K].

Frozen dough is a multicomponent multiphase system: below the initial freezing point, three phases must be considered with continuous changes in their relative fractions: dry substance, unfrozen water and ice crystals. Hence, determination of the real soluble solids is not trivial. Moreover, because of the low initial water content (x_{w0}), and because the fraction of salts really dissolved in the free water is unknown, the direct application of Raoult's law (i.e, the prediction of the initial freezing point using only the water mole fraction) would yield unreliable results. Schwartzberg (1976) proposed a modification of Raoult's law for nonideal systems, taking into account the water bound to the solids and therefore unavailable for freezing:

$$a_w = \frac{x_w - x_b}{x_w - x_b + \frac{M_w}{M_s}} \tag{4}$$

wherein x_w is the water mass fraction [g/g product] and x_b is the bound water mass fraction [g/g product].

In this paper, the constants a and b were determined by regression analysis from enthalpy curves obtained by DSC for each dough formulation. At the initial freezing point (T_f), with the application of Eq. (1) and Eq. (4) the following equation is obtained (Schwartzberg, 1977):

$$\frac{M_w}{M_s}x_s \cong -M_w(x_{w0} - x_b)\frac{LT_f}{RT_0^2} \tag{5}$$

wherein L is the ice fusion latent heat at 0 °C [322.9 J g^{-1}]. Finally, from the value of b determined with Eq. (2), it is possible to obtain the bound water fraction by comparison of Eqs. 5 and 3:

$$b = -(x_{w0} - x_b)LT_f \quad (6)$$

The unfreezable water content (x_u) at −40 °C was calculated as the difference between total water content (x_{w0}) and the amount of frozen water detected by the DSC fusion endotherm (Cogné et al., 2003; Hamdami et al., 2004), according to Eq. (7):

$$x_u = x_{w0} - \frac{\Delta_{fus}H}{L} \quad (7)$$

wherein $\Delta_{fus}H$ is the observed enthalpy change of water upon fusion (J g^{-1}).

The results for total water content (x_{w0}), fusion enthalpy ($\Delta_{fus}H$), unfreezable water fraction (x_u), bound water fraction (x_b), water activity (a_w) and initial freezing point (T_f) calculated by Eq. (1) are presented in Table 1.

Fusion enthalpies of formulations FI and FIII were significantly different, which may be ascribed to the different water contents of the bread dough. These values are in agreement with those previously reported by Matuda et al. (2005a), who found fusion enthalpy values varying from (86–89) J g^{-1} for bread dough with similar water contents (0.44 g/g of product).

The fraction of unfreezable water varied from 0.174 g/g of total product for formulation FIII to 0.182 g/g of total product for formulation FI. These values are slightly higher than those reported in previous studies (Laaksonen and Roos, 2000; Matuda et al., 2005a,b). The differences among these values can be attributed to the composition of the bread dough and to the different procedures in the studies. Laaksonen and Roos (2000) found an endothermic melting peak of ice having an onset temperature of −18 °C and an x_u value of (0.35 ± 0.00) g water/g solute. The authors suggested that this low value was probably due to the rather large amount of maltose, a disaccharide having two units of glucose, in the dough formulation. In this paper, DATEM, an anionic oil-in-water emulsifier, was added to the dough formulation. According to Rao et al. (1992), the presence of emulsifiers in dough may block the migration of moisture between gluten and starch, thereby preventing starch from taking up water.

Differences in unfreezable water found in this work, can also be attributed to different cooling rate. After rapid cooling, not only is a nonequilibrium system obtained below T_g, but also in a considerable temperature range above this transition (Bot, 2003; Slade and Levine, 1988).

Table 1
Water content (x_w), enthalpy of fusion (H_{fusion}), unfreezable water content (x_u), water activity (a_w) and initial freezing point (T_f) of French bread dough with different water contents.

Properties	F I	F II	F III	Tukey* 5%
x_{w0} (g/g of total product)	0.422 ± 0.002[a]	0.433 ± 0.001[b]	0.443 ± 0.001[c]	0.002
DSC curves				
$\Delta_{fus}H$ (J g^{-1})	80.55 ± 1.49[a]	85.60 ± 2.81[ab]	90.23 ± 1.68[b]	5.20
T_f (°C)	−5.27 ± 0.14[a]	−4.18 ± 0.49[a]	−4.43 ± 0.35[a]	1.50
x_u (g/g of total product)	0.182 ± 0.004[a]	0.178 ± 0.008[a]	0.174 ± 0.005[a]	0.012
x_b (g/g of total product)**	0.110	0.149	0.165	
Water activity				
a_w	0.949 ± 0.002[a]	0.950 ± 0.002[a]	0.952 ± 0.004[a]	0.008
T_f (°C)	−5.26 ± 0.24[a]	−5.23 ± 0.24[a]	−5.02 ± 0.42[a]	0.78
Time–Temperature curves				
T_f (°C)	−4.2	−3.4	−3.5	
T_t (°C)	−8.0	−7.3	−7.4	

* Means with the same letter are not significantly different ($P > 0.05$).
** Calculated from Eq. (6).

The bound water fraction of the dough formulations varied from (0.110–0.165) g/g of total product, increasing as initial water content increased. One possible explanation is that the larger the amount of water available, the larger the amount of water that can be absorbed in the amorphous regions of starch in the mass – and this absorbed water has a lower mobility. The values found in this paper are comparable to those reported by Cleland and Valentas (1997); these authors suggest adopting x_b for bread from (0.09–0.16) g/g of total product.

Water activity (a_w) was not significantly influenced by the amount of water in the bread dough. As water activity is the only experimental parameter that influences the calculation of initial freezing point (Eq. (1)), no variation in initial freezing point was thus expected for any of the studied formulations with different water contents in the bread dough – and the values of initial freezing point obtained by DSC were not significantly different.

The differences between freezing and thawing curves are apparent in Fig. 2, which shows dough pieces that were frozen and thawed under comparable conditions. Cooling to the initial freezing point ($T_f = -3.4$ °C) and complete freezing required approximately 120 min for formulation FII, whereas warming to initial thawing point ($T_t = -7.3$ °C) and completely melting the ice required approximately 85 min. The thawing curve is not merely a reversed freezing curve, and the differences come from the fact that the thermal conductivity and thermal diffusivity of the dough are higher in the frozen state than in the thawed state.

The initial freezing point (T_f) obtained from the cooling curves is around 1.5 °C higher than those calculated by water activity (Table 1). The discrepancy among different methods was also reported by Wang and Kolbe (1991); it may be attributed to factors such as the thermocouple position in the bread dough cylinder, the thermocouple time response and extrapolation of curve fragments in time–temperature curves. The calculation of the initial freezing point through Eq. (1) is simpler than from the cooling curves, and thus, for the objective of determining the freezing point depression, the use of water activity data along with Eq. (1) is preferable.

Salvadori and Mascheroni (1991) developed a simplified analytical model for the prediction of freezing and thawing times of foods, based on an equation relating the temperature at the center of the food to a dimensionless variable that takes into account the simultaneous influence of time, process parameters, thermophysical properties and size of product:

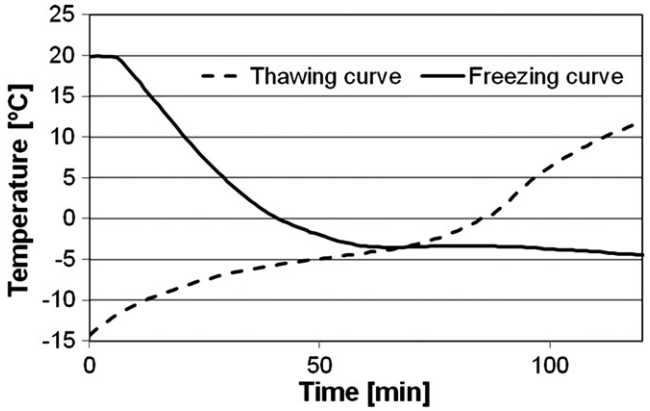

Fig. 2. Temperature–time curves of the center of dough pieces (FII, initial water content: 0.433 g/g total product) during freezing and thawing under comparable circumstances and respective predictive models.

$$t_f = (AT + B)\left(\frac{1}{Bi} + c\right)\left[\frac{\left(T_f - T_i\right)}{T_f}\right]^n\left[\frac{\left(T_{amb} - T_f\right)}{T_f}\right]^{-m}\frac{r^2}{\alpha} \quad (8)$$

$$t_t = (AT + B)\left(\frac{1}{Bi} + c\right)\left[\frac{\left(T_i - T_f\right)}{T_f}\right]^n\left[\frac{\left(T_f - T_{amb}\right)}{T_f}\right]^{-m}\frac{r^2}{\alpha} \quad (9)$$

$$2 \le T_i \le 25\ ^\circ\mathrm{C} \quad 5 \le T_{amb} \le 45\ ^\circ\mathrm{C} \quad \text{or} \quad -40 \le T_{amb} \le -20\ ^\circ\mathrm{C} \quad 1 \le Bi \le 44$$

wherein t_f is the freezing time [s], t_t is the thawing time [s], T is the thermal center temperature [°C], T_f is the initial freezing point [°C], T_i is the initial temperature [°C], T_{amb} is the ambient temperature [°C], r is the characteristic dimension [m], α is the thermal diffusivity of fresh food [$m^2\ s^{-1}$] and Bi is the *Biot* number. A, B, c, n and m are constants dependent on process and food geometry.

The authors compared the predicted freezing and thawing times to experimental data reported in the literature for various types of food and found a mean absolute percentage error of 5% and 4.2% for freezing and thawing times, respectively.

Predicted freezing and thawing times calculated through Eqs. 8 and 9 by nonlinear regression (the Marquardt algorithm), constant values and calculated process parameters are shown in Table 2. The considered thermal conductivity and thermal diffusivity of unfrozen dough were 0.405 W m^{-1} °C^{-1} and 1.3 × 10^{-7} m^2 s^{-1}, respectively (Matuda, 2008). For both freezing and thawing predictive models, good estimations were obtained and they can be applied with the same accuracy to working conditions other than those used in this paper.

It was not possible to identify glass-transition temperatures in spite of the chosen heating rate. Laaksonen and Roos (2000) did not find a second-order transition in frozen bread dough through DSC either; these authors attributed this failure to either the sensitivity of the equipment or the chosen heating rate.

3.2. Modeling

The heating rate of 5 °C min^{-1} was chosen due to its suitability for observing glass-transition temperatures. Nevertheless, this is a rather high heating rate, which may generate temperature lags (Fasina, 2005) – a critical occurrence in first-order phase transitions, as they may affect the detection of the onset of these phenomena. Therefore, apparent specific heat curves were corrected according to the procedure developed by Wang and Kolbe (1991). These authors reported that these curves may be distorted because of the slow time response of dynamic calorimetry and proposed the following first-order correction:

$$Cp^*_{app}(T) = Cp_{app}(T) + \tau\frac{\mathrm{d}Cp_{app}(T)}{\mathrm{d}t} \quad (10)$$

wherein Cp_{app} is the value determined by DSC analysis and τ describes the delay of the sample response [s], which can be determined through an iterative procedure in which the corrected enthalpy is assumed to have the same value as the experimental enthalpy. In Fig. 3 the DSC curves with and without the first-order correction of Wang and Kolbe (1991) are presented for formulation FI, and the freezing point is the T_{peak} of the DSC raw data. The shape of specific heat curves obtained in this study is typical of results reported in the literature for bread dough, such as those of Lind (1991).

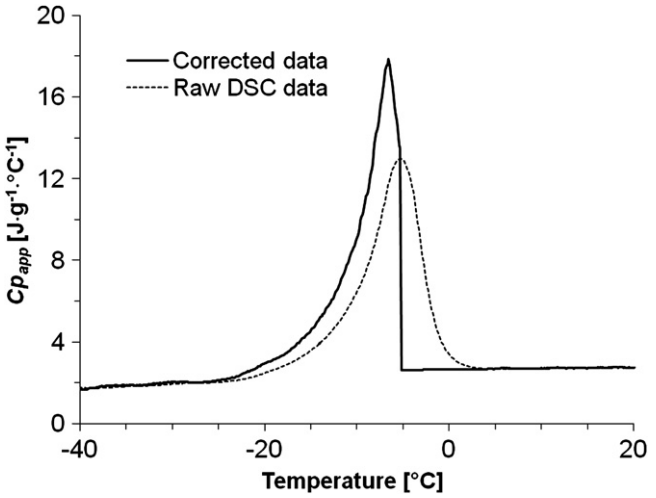

Fig. 3. DSC curves with and without the dynamic correction proposed by Wang and Kolbe (1991) for formulation FI (initial water content: 0.422 g/g total product).

ANOVA ($p < 0.05$) was applied to the corrected Cp_{app} results as a function of temperature and total water content. For above the initial freezing temperature, Cp_{app} values varied from (2.549–2.840) J g^{-1} °C^{-1} and significant differences between bread dough formulations were observed. Therefore, a fitted model was obtained by a multiple linear regression ($r^2 = 0.923$):

$$Cp_{app,unf} = (2.984 - 0.834x_{w0} + 0.007T) \pm 0.020 \quad 0.422 \le x_{w0} \le 0.443\ \mathrm{g/g\ product} \quad -5.2 \le T \le 31.5\ ^\circ\mathrm{C} \quad (11)$$

Below the initial freezing point, values of heat capacity of foods can be estimated using either semi-theoretical equations that are based on the thermodynamic principles of the freezing point depression or empirical equations that are derived from analyses of experimental data (Baik et al., 2001; Ngadi et al., 2003). Some authors have developed semi-theoretical equations expressing apparent specific heat as a function of temperature and moisture content for bakery products.

From corrected data values three specific heat models were correlated. The first one was the additive model (Cogné et al., 2003), based on the assumption that the thermal contribution of each pure component is maintained upon mixing:

$$Cp_{app} = \sum x_j Cp_j - L\left(T_f\right)\frac{\mathrm{d}x_l(T)}{\mathrm{d}T} \quad L\left(T_f\right) = 333.802 + 2.1165\,T \quad (12)$$

Table 2
Values of constants obtained by nonlinear regression for prediction of freezing and thawing times of bread dough as well as thermophysical properties and process parameters of fresh dough.

Constants*	A	B	c	n	m	r^2
Freezing	−0.506	0.464	0.241	0.151	0.600	0.937
Thawing	0.144	3.158	0.045	−0.057	0.335	0.942
Process parameters	h [W·m^{-2} °C^{-1}]	T_{amb} [°C]	T_i [°C]	Bi	t_{exp} (min)	t_{pred} (min)
Freezing	25	−18	20	1.39	120	115
Thawing	25	18	−15	1.39	85	79

* Predictive models:Freezing: $t_f = (AT + B)(\frac{1}{Bi} + c)\ [\frac{(T_f - T_i)}{T_f}]^n [\frac{(T_{amb} - T_f)}{T_f}]^{-m}\frac{r^2}{\alpha}$; Thawing: $t_t = (AT + B)(\frac{1}{Bi} + c)\ [\frac{(T_i - T_f)}{T_f}]^n [\frac{(T_f - T_{amb})}{T_f}]^{-m}\frac{r^2}{\alpha}$

wherein the subscript j represents the different components (lipid, protein, carbohydrate, water or ice), x_j is their mass fraction, C_{Pj} is their intrinsic heat capacity as published by Choi and Okos (1986), x_I is the ice mass fraction and T_f is the initial freezing point. The term $dx_I(T)/dT$ was calculated using Raoult's model (Eq. (13)) and the pure ice fusion latent heat, $L(T_f)$, was calculated as a function of temperature.

$$x_I = (x_{w0} - x_b)\left(1 - \frac{T_f}{T}\right) \tag{13}$$

Chen's and Schwartzberg's models, which were also applied, are based on Raoult's law. Chen (1985) modified the Bartlett thermodynamic method based on experimental data derived from Mollier diagrams for bread:

$$Cp_{app} = 4.18 \times (0.50 - 0.3x_s) + \frac{x_s}{M_s}\frac{RT_0^2}{T^2} \tag{14}$$

Schwartzberg (1976) developed one of the simplest models based on Eq. (13), and assuming that component heat capacities are constant with temperature,

$$Cp_{app} = Cp_{app,unf} - (x_{w0} - x_b)\left(\frac{LT_f}{T^2} + Cp_w - Cp_I\right) \tag{15}$$

A modification was introduced into Schwartzberg's model, in which the heat capacity of unfrozen bread dough was considered dependent on temperature and moisture content, since it is a product with an intermediate water content and most models provide accurate prediction only for high moisture foods. Thus, the following modification of Schwartzberg's model is proposed:

$$Cp_{app} = Cp_{app,unf}(T, x_{w0}) - (x_{w0} - x_b)\left(\frac{LT_f}{T^2} + Cp_w - Cp_I\right) \tag{16}$$

wherein $Cp_{app,unf}(T,x_{w0})$ is calculated from Eq. (11).

Fig. 4 shows the parity chart of calculated specific heat (Cp_{app}) from the additive, Chen and modified Schwartzberg models as a function of corrected values of experimental data. For the additive model, the value of specific heat of bread solids (Cp_s) reported by Baik et al. (2001) was used. The term x_s/M_s present in Chen's predictive model was calculated according to Cogné et al. (2003).

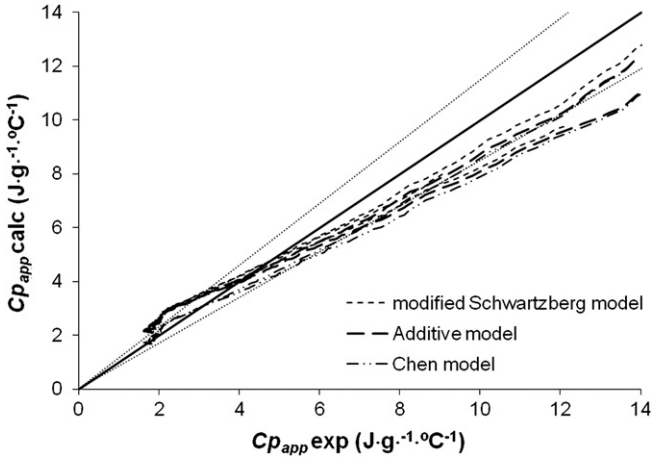

Fig. 4. Parity chart of predicted specific heat of frozen bread dough (Cp_{app}calc) obtained by the additive, Chen and modified Schwartzberg models in comparison to the experimental data (Cp_{app}exp).

The Marquardt algorithm was used to correlate model parameters as a function of temperature and water content using experimental data for below T_f. The best fit was achieved from the modified Schwartzberg model ($r^2 = 0.905$), whereas for the Chen and the additive models, the adjusted correlations were 0.797 and 0.770, respectively. The specific heat values greater than 8 J g^{-1} C^{-1} had larger deviations. In fact, it is observed that these values correspond to the region of phase change, wherein the latent heat component becomes predominant.

The frozen water fraction and bound water fraction are extremely important parameters for the design of the freezing process and determination of shelf life under frozen storage of dough. Predictive models for the determination of bound water fraction, initial freezing point and thawing point were proposed based on experimental data. The information presented in this study can be helpful for simple and rapid engineering calculations in the design of a freezing process for bread dough.

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